

Chemical Trend of Superconducting Transition Temperature in Hole-doped Delafossite of CuAlO_2 , AgAlO_2 and AuAlO_2

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Abstract

We have performed the first-principles calculations about the superconducting transition temperature T_c of hole-doped delafossite CuAlO_2 , AgAlO_2 and AuAlO_2 . Calculated T_c are about 50 K(CuAlO_2), 40 K(AgAlO_2) and 3 K(AuAlO_2) at maximum in the optimum hole-doping concentration. The low T_c of AuAlO_2 is attributed to the weak electron-phonon interaction caused by the low covalency and heavy atomic mass.

Keywords: A. Semiconductors; C. Delafossite structure; D. Electron-phonon interactions; E. Density functional theory

1. Introduction

CuAlO_2 has a delafossite structure (Fig. 1) and a two-dimensional electronic structure caused by the natural super-lattices of O-Cu-O dumbbell. Kawazoe *et al.* have found that the CuAlO_2 is p -type transparent conducting oxides (TCO) without any intentional doping.[1] Nakanishi *et al.* studied the pressure dependence of the structures [2] and the role of the self-interaction correction in CuAlO_2 . [3] Transparent p -type conductors such as CuAlO_2 are important for the p - n junction of TCO and a realization of high-efficiency photovoltaic solar-cells. First-principles calculations have shown the possibility of applications for high efficiency thermoelectric power with about 1% hole-doping. [4, 5, 6]

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Katayama-Yoshida *et al.* have simulated the Fermi surface of the p -type doped CuAlO_2 by shifting the Fermi level rigidly and proposed that the nesting Fermi surface may cause a strong electron-phonon interaction and a transparent superconductivity for visible light. [7] But, the calculation of superconducting transition temperature T_c was not carried out. In previous study, we calculated the T_c of p -type doped CuAlO_2 [8] and found that the T_c goes up to about 50 K due to the strong electron-phonon interaction by the two dimensional flat valence band. The origin of the flat band is the π -band of hybridized O $2p_z$ and Cu $3d_{3z^2-r^2}$ on the frustrated triangular lattice in the two dimensional plane. It is very interesting to see the relation between the T_c and the flatness of the flat band by changing the Cu $3d_{3z^2-r^2}$, Ag $4d_{3z^2-r^2}$ and Au $5d_{3z^2-r^2}$. In this study, we performed the calculation of T_c and the electron-phonon interaction about the chemical trend of p -type doped CuAlO_2 , AgAlO_2 and AuAlO_2 .

2. Calculation Methods

The calculations were performed within the density functional theory[9, 10] with a plane-wave pseudopotential method, as implemented in the Quantum-ESPRESSO code.[11] We employed the Perdew-Wang 91 generalized gradient approximation (GGA) exchange-correlation functional[12] and ultra-soft pseudopotentials.[13] For the pseudopotentials, 3d electrons of transition metals were also included in the valence electrons. In reciprocal lattice space integral calculation, we used $8 \times 8 \times 8$ (electron and phonon) and $32 \times 32 \times 32$ (density of states and average at Fermi level) \mathbf{k} -point grids in the Monkhorst-Pack grid.[14] The energy cut-off for wave function was 40 Ry and that for charge density was 320 Ry. These \mathbf{k} -point meshes are fine enough to achieve convergence within 10 mRy/atom in the total energy.

The delafossite structure belongs to the space group $R\bar{3}m$ (No.166) and is represented by cell parameters a and c , and internal parameter z (See Fig. 1). These cell parameters and internal parameter were optimized by the constant-pressure variable-cell relaxation using the Parrinello-Rahman method[15] without any symmetry requirements.

In this study, some properties of hole-doped materials are approximated because it is difficult for first-principles calculation to deal with the doped system exactly. Let's take the electron-phonon interaction λ for example. λ is defined as follows:

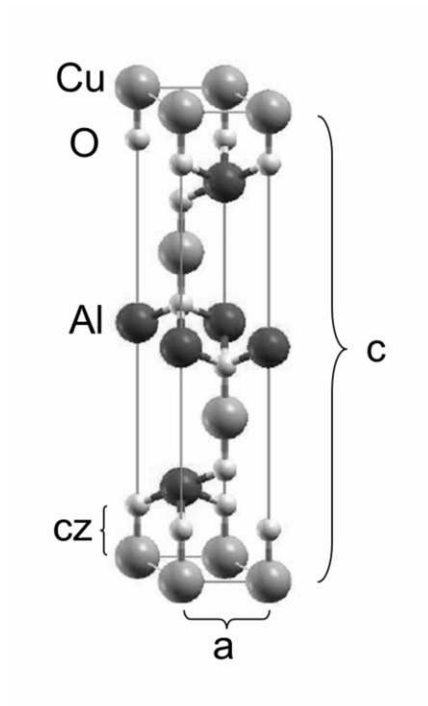


Figure 1: The crystal structure of delafossite CuAlO_2 .

$$\lambda = \sum_{\nu\mathbf{q}} \frac{2N(\varepsilon_F) \sum_{\mathbf{k}} |M_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\nu\mathbf{q}}|^2 \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}} - \varepsilon_F)}{\omega_{\nu\mathbf{q}} \sum_{\mathbf{k}\mathbf{q}'} \delta(\varepsilon_{\mathbf{k}} - \varepsilon_F) \delta(\varepsilon_{\mathbf{k}+\mathbf{q}'} - \varepsilon_F)}. \quad (1)$$

(1) For the non-doped systems, we calculated the dynamical matrix, the phonon frequency $\omega_{\nu\mathbf{q}}$ and the electron-phonon matrix $M_{\mathbf{k},\mathbf{k}+\mathbf{q}}^{\nu\mathbf{q}}$. (2) For the doped systems, we calculated the Fermi level ε_F and the density of states at the Fermi level $N(\varepsilon_F)$ with the number of valence electrons reduced using the eigenvalues $\varepsilon_{\mathbf{k}}$ of the non-doped system. (3) By using the results of (1) and (2), we calculated the electron-phonon interaction λ and the other superconducting properties. This approximation is based on the idea that the doping does not greatly change electron and phonon band structures. In this study, we show the results of 0.1 \sim 1.0 hole-doped systems.

We calculated the superconducting transition temperature by using the Allen-Dynes modified McMillan's formula.[16, 17] According to this formula, T_c is given by three parameters: the electron-phonon interaction λ , the logarithmic averaged phonon frequency ω_{\log} , and the screened Coulomb interaction μ^* , in the following form.

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left(\frac{-1.04(1 + \lambda)}{\lambda - \mu^*(1 + 0.62\lambda)} \right). \quad (2)$$

$$\omega_{\log} = \exp \left(\frac{2}{\lambda} \int_0^\infty d\omega \frac{\alpha^2 F(\omega)}{\omega} \log \omega \right). \quad (3)$$

Here, $\alpha^2 F(\omega)$ is the Eliashberg function. λ and ω_{\log} are obtained by the first-principle calculations using the density functional perturbation theory.[18] As for μ^* , we assume the value $\mu^* = 0.1$. This value holds for weakly correlated materials.

3. Calculation Results and Discussion

Before superconducting calculation, we optimized the cell parameters. The optimization results show that the structural transition does not occur and the delafossite structure is stable. Table 1 shows the optimized cell parameters. The distance between transition metal and oxygen is the longest in CuAlO_2 . This shows the strong covalency of CuAlO_2 . The calculation results of CuAlO_2 agree very well with the experimental data ($a = 2.858\text{\AA}$, $c/a = 5.934$ and $z = 0.1099$ [19, 20]).

	CuAlO ₂	AgAlO ₂	AuAlO ₂
a [Å]	2.859	2.895	2.913
c/a	5.965	6.369	6.373
z	0.1101	0.1148	0.1158

Table 1: The optimized cell parameters.

Fig. 2 shows the calculated results of electron-phonon interaction λ . AuAlO₂ has lower λ than CuAlO₂ and AgAlO₂. On the other hand, λ of AgAlO₂ is close to that of CuAlO₂. This difference is attributed to not only atomic mass but also covalency.

Fig. 3 and 4 show the band structure, the density of states and energy gaps. The energy gaps are 1.83eV(CuAlO₂), 1.47(AgAlO₂) and 0.46(AuAlO₂). As d -wave function extends ($3d \rightarrow 4d \rightarrow 5d$), the d -band widen and the covalent bonding weaken. So this low covalency of AuAlO₂ is the cause of his low electron-phonon interaction λ . It is also clearly seen in Fig. 3 that the flatness of the top of the valence band decreases from CuAlO₂ to AuAlO₂ with reducing the covalency.

Fig. 5 shows the calculated results of logarithmic averaged phonon frequency ω_{\log} . These are almost constant for the number of holes. CuAlO₂ has the highest ω_{\log} . The difference of ω_{\log} is due to atomic mass of transition metals.

Fig. 6 shows the calculated results of T_c . The lightly hole-doped material ($N_h = 0.2 \sim 0.3$) has higher T_c while the heavily doped material ($N_h = 0.6 \sim 1.0$) has lower T_c . AgAlO₂ has a little lower T_c than CuAlO₂. On the other hand, AuAlO₂ has much lower T_c than these due to the heavy atomic mass and the low covalency mentioned above.

4. Conclusions

In summary, we calculated the chemical trend of superconducting transition temperature of the hole-doped delafossite CuAlO₂, AgAlO₂ and AuAlO₂. Calculated T_c are about 50 K(CuAlO₂), 40 K(AgAlO₂) and 3 K(AuAlO₂) at maximum. The low T_c of AuAlO₂ is attributed to low covalency and heavy atomic mass.

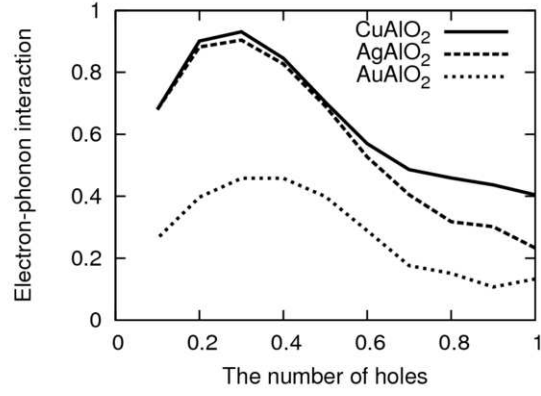


Figure 2: Electron-phonon interaction λ .

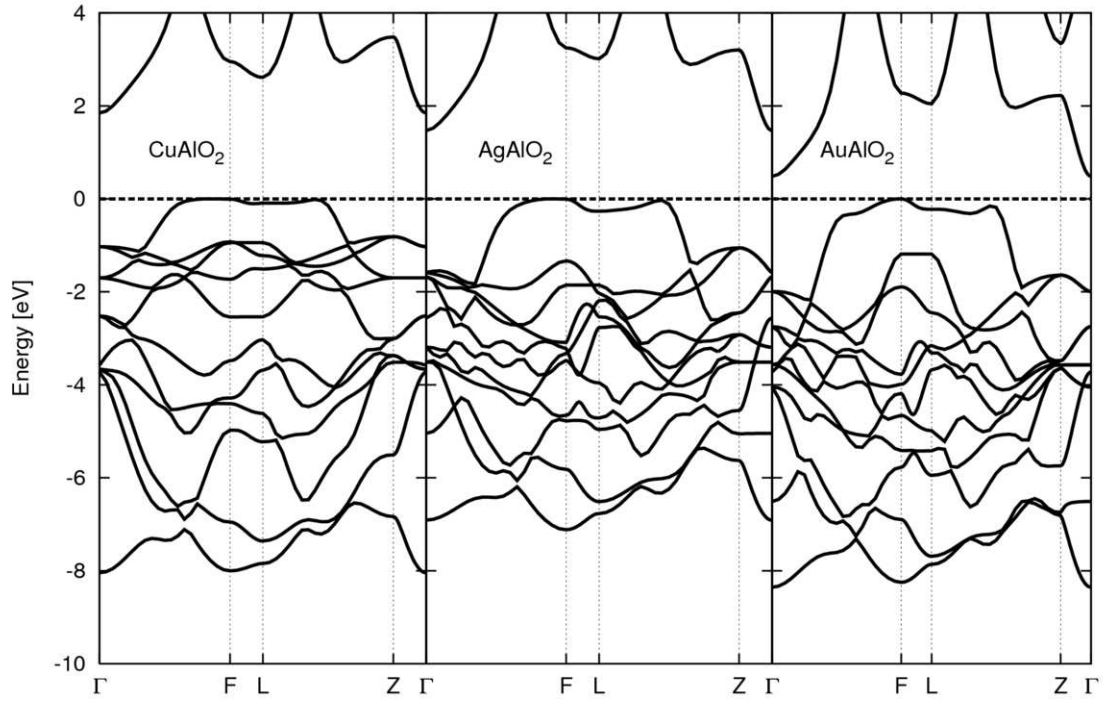


Figure 3: Band structures of CuAlO₂(left), AgAlO₂(center) and AuAlO₂(right).

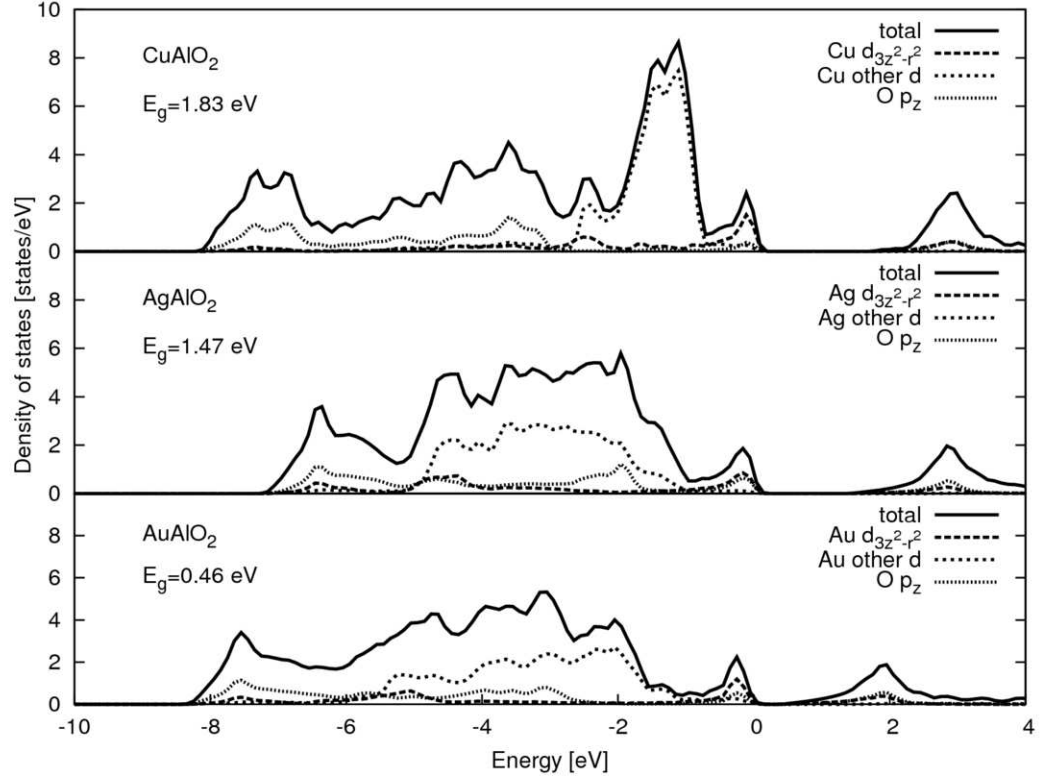


Figure 4: Density of states and energy gaps.

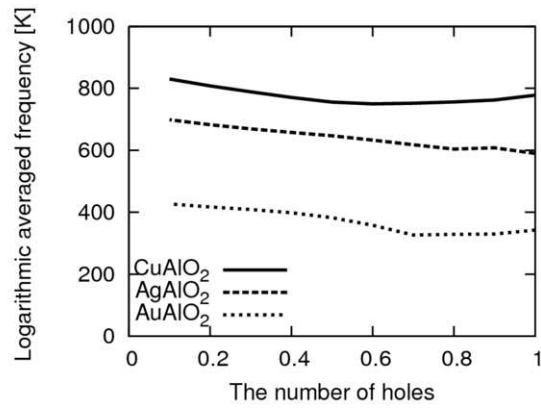


Figure 5: Logarithmic averaged phonon frequency ω_{\log} .

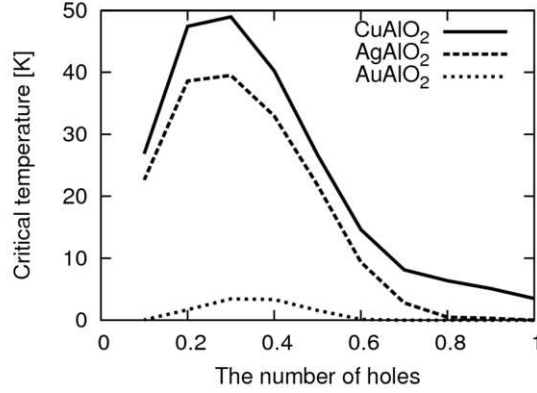


Figure 6: Superconducting transition temperature T_c .

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